Measurements of the Efficiency of a NASA/Air Force Alkaline Scrubber in Removing Waste NO$_2$/N$_2$O$_4$ Vapors

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MEASUREMENTS OF THE EFFICIENCY OF A NASA/AIR FORCE ALKALINE SCRUBBER IN REMOVING WASTE NO$_2$/N$_2$O$_4$ VAPORS

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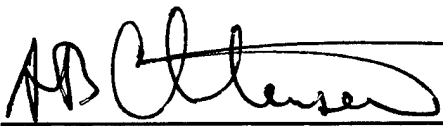Prepared for

MEASUREMENTS OF THE EFFICIENCY OF A
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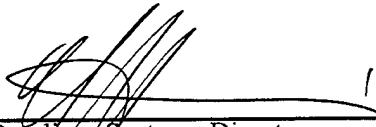REMOVING WASTE NO_2/N_2O_4 VAPORS

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ABSTRACT

An alkaline scrubber was installed at Vandenberg Air Force Base's Hypergolic Storage Facility (HSF) in late 1991 to remove waste N_2O_4/NO_2 vapors in nitrogen diluent. A test was run on 13 December 1991 to determine this scrubber's efficiency. Measurements were made with the nitrogen diluent flowing at about 53 SCFM (standard cubic feet per minute) and at about 90 SCFM. The mole fractions of NO_x and NO entering and leaving the scrubber were repeatedly measured in real time with a chemiluminescent analyzer. The mole fraction of NO_x entering the scrubber was between 250,000 and 280,000 ppm in nitrogen. The mole fraction of NO_x leaving the scrubber and vented into the atmosphere increased with increasing diluent flow rate. The measured mole fraction of NO_x in the exhaust stream was 870 ppm when the nitrogen flow was 53 SCFM and 1675 ppm when the nitrogen flow was about 90 SCFM. The scrubber's performance matched that of similar scrubbers tested elsewhere. Over 99% of the N_2O_4/NO_2 vapors were scrubbed even when the nitrogen diluent flow was 90 SCFM. Nevertheless, the maximum diluent gas flow through the scrubber has been limited to about 53 SCFM in accordance with the requirement set by the Santa Barbara Air Pollution Control District that the scrubber's exhaust plume be colorless.

Air pollution regulations in Santa Barbara County require that the performance of the scrubbers at Vandenberg Air Force Base be remeasured every few years. Past performance measurements made by others have been highly inaccurate. This report discusses how to accurately measure both the amount of nitrogen oxides that enters the scrubber and the amount that leaves the scrubber and is exhausted into the atmosphere.

Scrubber chemistry is discussed quantitatively in some detail. As is illustrated in this report, a knowledge of scrubber chemistry is often essential in assessing the accuracy of scrubber performance measurements.

ACKNOWLEDGMENTS

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1. INTRODUCTION

Titan launch vehicles and the Space Shuttle have rockets powered by the hypergolic reaction of liquid nitrogen tetroxide (N_2O_4) with hydrazine fuels (N_2H_4, CH_3NHNH_2, $(CH_3)_2NNH_2$). At Vandenberg Air Force Base and at Cape Canaveral Air Station, the rockets are loaded with the hypergols (N_2O_4 oxidizer and hydrazine fuels) at the launch site. The hypergols are stored in large tanks not far from the launch site. Some of the hypergols, unavoidably, end up as waste, for example, as vapors that are left in transfer lines or that pass through the vent in a storage tank while the tank is being filled. Waste N_2O_4 is chemically destroyed at Kennedy Space Center (KSC), Cape Canaveral Air Station (CCAS) and Vandenberg Air Force Base (VAFB) by passing N_2O_4 vapors through a packed-column scrubber containing an alkaline scrubbing liquor. This scrubber is often called by the Air Force the OVSS or the Oxidizer Vapor Scrubber System. Previously at several launch sites, waste N_2O_4 vapors were thermally decomposed by passing them through a burner, but this method has been abandoned as nitric oxide (NO) is produced in the burner and is vented into the atmosphere. Both NO and N_2O_4 vapors are toxic. Packed-column alkaline scrubbers have always performed reliably and efficiently. In 1991, such a scrubber was installed at VAFB's Hypergolic Storage Facility (HSF). [This facility was formerly and erroneously named the Hypergolic Stockpile Storage Facility (HSSF).] The measurements reported here were made as part of an effort to verify that this alkaline scrubber performs as expected.

2. DESCRIPTION OF SCRUBBER

The Oxidizer Vapor Scrubber System (which in this report is called an alkaline scrubber or simply the scrubber) was built in Denver by the Martin Marietta Corporation. Figure 1 is a photograph of a scrubber identical to the scrubber at the HSF; this photograph was taken in Denver just before the scrubber was shipped to the Air Force. The scrubber installed at the HSF consists of four packed-bed towers, which are connected in series, a 850-gallon storage or sump tank for holding the alkaline scrubbing liquor, and a pump for circulating the liquor. Each tower is 30 inches in diameter. The first three towers are packed with ⅝-inch polypropylene pall rings (Koch Engineering Flexirings®) to a height of about 4.3 ft. The fourth tower contains structured Sulzer packing, also from Koch Engineering. Scrubbing liquor is pumped at a rate of 200 gal/min (or an average of 50 gal/min per tower) from the sump tank through four spray nozzles, one at the top of each tower. The liquor trickles down through the packing, keeping it wet, and flows by gravity back into the sump tank. The N_2O_4 vapors, mixed with varying amounts of nitrogen N_2, flow through each tower in succession in a direction opposite to the liquor flow. The gas flow rate, which is regulated by an orifice upstream of the scrubber, can be as great as 400 standard cubic feet per minute (SCFM). The gas leaving the scrubber could contain as much as a few thousand parts per million (ppm) nitrogen oxide vapor. This gas is vented to atmosphere at a height of about 75 ft above ground and at a distance of about 120 ft away from the scrubber.

In the gas phase and in aqueous solutions, N_2O_4 largely dissociates into nitrogen dioxide NO_2, a dark brown, toxic gas:

$$N_2O_4 \rightleftarrows 2NO_2. \tag{1}$$

Reaction 1 and its reverse (termed reaction -1) are very rapid, so that under all conditions of interest

$$[NO_2]^2/[N_2O_4] = K_1, \tag{2}$$

where K_1 is the temperature-dependent equilibrium constant, and the brackets denote molar concentration. In the gas phase at 25°C, $K_1 = 5.96 \times 10^{-3}$ mol/L, and in dilute aqueous solutions at 25°C, $K_1 = 1.4 \times 10^{-5}$ mol/L. See Ref. 1 for a further discussion.

Gaseous N_2O_4 and NO_2 both dissolve in the aqueous scrubbing liquor, and one or both of these species reacts with water to form nitric and nitrous acid (HNO_3 and HNO_2):
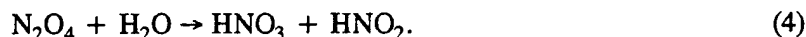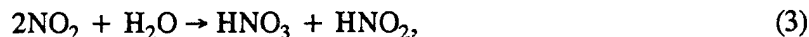
$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2, \tag{3}$$

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2. \tag{4}$$

It has been impossible to determine experimentally which of these two reactions is more important, because the reaction products are the same and because the N_2O_4 concentration is always proportional
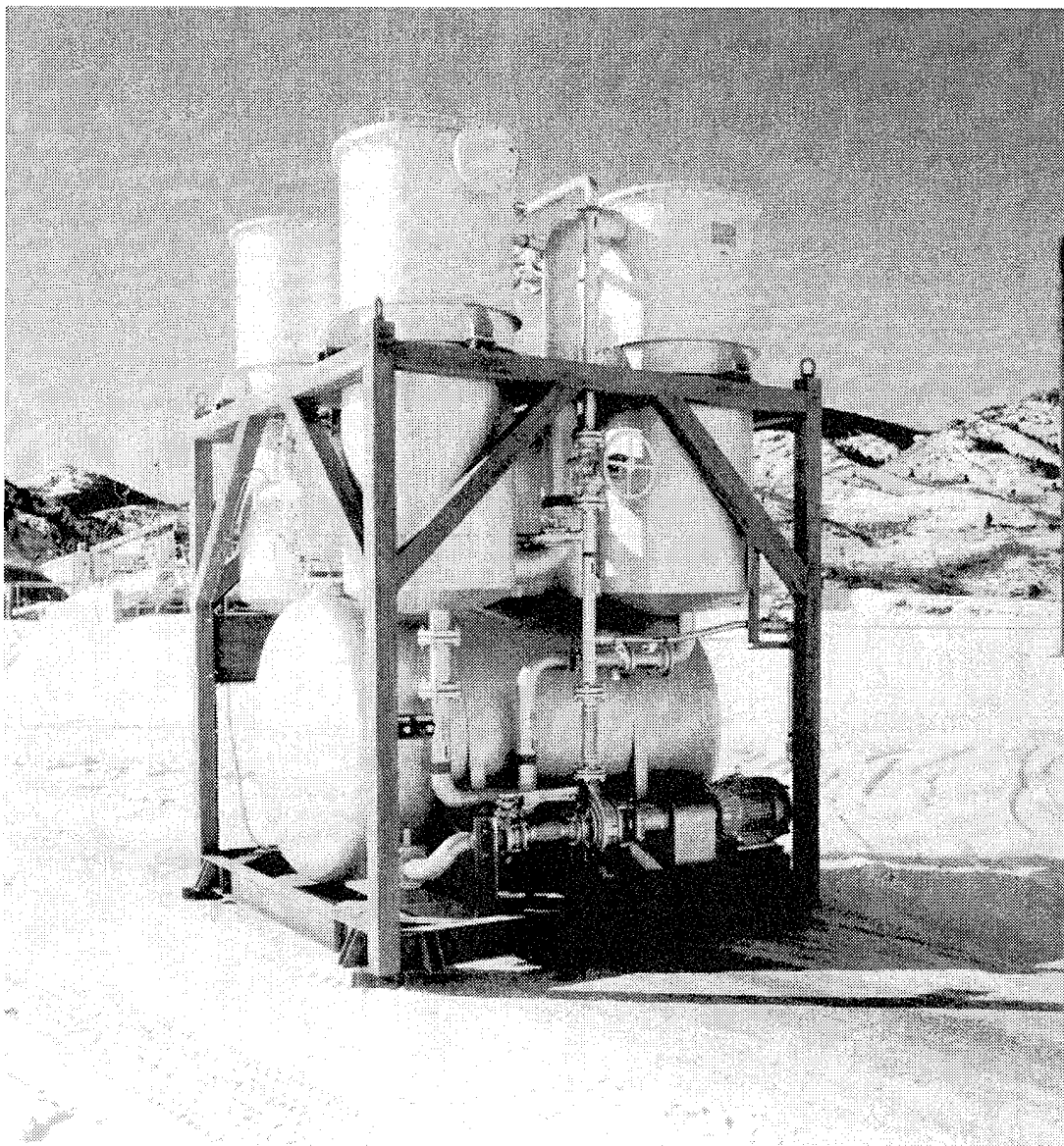
Figure 1. A photograph of an Oxidizer Vapor Scrubber System (OVSS) before shipment to VAFB. The large horizontal tank at the bottom is the sump tank, which holds the scrubbing liquor (an aqueous solution initially containing 25 wt% NaOH). The four vertical tanks or towers (three of which are clearly visible in the photograph) are the packed-column scrubbers. These towers are 30 inches in diam and 6.5 feet high. The pump that raises the scrubbing liquor from the sump tank to the top of each tower is in front of the sump tank, connected to an electric motor that powers it. The pump operates continuously whenever the scrubber is in use. At the Hypergolic Storage Facility, gas streams containing N_2O_4 vapors enter near the bottom of the first tower and exit through a 4-inch-diam pipe near the top of the fourth tower. Greater than 99% of the N_2O_4 vapors are removed by the scrubber under typical HSF operating conditions. The OVSS in this photograph has its exit port blanked off; at VAFB, the exit is connected to an exhaust duct that carries the gas away from the scrubber before discharging it into the atmosphere.

to the square of the NO_2 concentration (see Eq. 2). This means that the removal of NO_2 via reaction 3 is equivalent to the removal of N_2O_4 via reaction 4, and vice versa. For either reaction, the rate of scrubbing is proportional to the square of the NO_2 concentration.[1] Consequently, the rate of NO_2 scrubbing is 10^4 times faster when the NO_2 concentration is 100,000 ppm than when it is 1000 ppm. Scrubbing is rapid at high NO_2 concentrations (> 10,000 ppm), but slow at low NO_2 concentrations (< 1000 ppm). Previous measurements[2-5] were made on NASA/AirForce scrubbers similar to the one installed at HSF. These measurements show that these scrubbers are capable of reducing the concentration of waste N_2O_4/NO_2 vapors from very high concentrations to less than 5000 ppm when the gas flow rate out of the scrubber (which is almost entirely nitrogen diluent) does not exceed 200 SCFM.

The scrubbing liquor used in the oxidizer scrubbers is an aqueous solution initially containing 8 mol/L sodium hydroxide NaOH (25 wt% NaOH). The NaOH, which makes the scrubbing liquor alkaline, is added because the nitrous acid produced in reactions 3 and 4 is unstable. Nitrous acid, in high concentrations, disproportionates into nitric acid and nitric oxide:

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O. \tag{5}$$
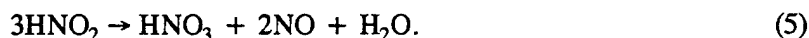
Nitric oxide is a toxic gas. Sodium hydroxide reacts with nitrous acid as rapidly as it is formed to produce dissolved sodium nitrite $NaNO_2$, which is stable as long as the solution remains alkaline:

$$NaOH + HNO_2 \rightarrow NaNO_2 + H_2O. \tag{6}$$
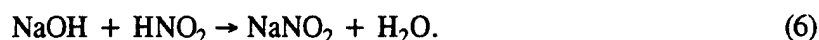
The liquid N_2O_4 used in Titan rockets contains about 1 wt % dissolved nitric oxide; the attitude control rockets on the Shuttle uses liquid N_2O_4 with 3 wt % NO dissolved in it. Nitric oxide dissolves in liquid N_2O_4 by reacting with the N_2O_4 to produce N_2O_3:

$$NO(soln) + \tfrac{1}{2} N_2O_4(soln) \rightarrow N_2O_3(soln) \tag{7}$$
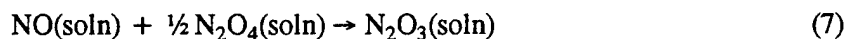
where (soln) denotes a dissolved species. Nitric oxide does not dissolve completely in liquid N_2O_4; some remains in the gas phase. In the gas phase (and also in aqueous solution), a portion of the NO reacts with NO_2 to produce N_2O_3:

$$NO + NO_2 \rightleftarrows N_2O_3 \tag{8}$$

Reaction 8 and its reverse are very rapid, so that under all conditions of interest, both in the gas phase and in aqueous solution,

$$[N_2O_3]/[NO][NO_2] = K_8 \tag{9}$$

where K_8 is the temperature-dependent equilibrium constant for reaction 8.

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The scrubber removes gaseous nitric oxide by one or both of the following aqueous-phase reactions
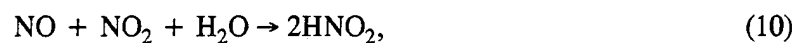
$$NO + NO_2 + H_2O \rightarrow 2HNO_2, \tag{10}$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2. \tag{11}$$

It has been impossible to determine experimentally which of these two reactions is more important, because the reaction products are the same and because the N_2O_3 concentration is always proportional to the product of the NO and NO_2 concentrations (see Eq. 9). Reference 1 contains a more thorough discussion of NO/NO_2 aqueous-phase chemistry.

3. DESCRIPTION OF MEASUREMENTS

A Thermal Electron Corporation (TECO) model 10 chemiluminescent analyzer was used to measure the mole fractions of NO and NO_X in the gas stream entering and exiting the scrubber. Mole fractions of pollutants such as NO, NO_2, and NO_X are customarily given in parts per million (ppm). The mole fraction of NO_X is defined to be equal to the value that the sum of the mole fractions of NO and NO_2 would have if all the N_2O_3 and N_2O_4 were dissociated into NO and NO_2, that is,

$$x_{NOX} = (x_{NO} + x_{NO2} + 2x_{N2O3} + 2x_{N2O4})/(1 + x_{N2O3} + x_{N2O4}) \qquad (12)$$

where x_B is the mole fraction of substance B. The chemiluminescent analyzer also detects nitric acid, either in the gas phase or in aerosols, as NO_X. In air pollution studies, where NO_2 mole fractions are low and N_2O_3 and N_2O_4 mole fractions are even lower (that is, $x_{N2O3} + x_{N2O4} << 1$), Eq. 12 is often written with the denominator, $1 + x_{N2O3} + x_{N2O4}$, set to unity. The approximation $x_{N2O3} + x_{N2O4} << 1$ is not valid, however, when discussing the composition of the vapor above liquid N_2O_4.

Often it is said that a measurement of NO_X in ppm is a concentration measurement. This terminology is not used in this report, because it is inaccurate. Concentration refers to amount per volume, for example, moles of substance per liter (mol/L). The chemiluminescent analyzer does not measure concentrations, but rather it measures mole fractions or what is equivalent, parts per million by volume.

The chemiluminescent analyzer drew in samples of the gas entering and exiting the scrubber through gas sampling ports especially built into the scrubber for this purpose. A real-time chemiluminescent measurement is an EPA-approved method of measuring the mole fractions of NO and NO_X,[6] and a properly calibrated chemiluminescent analyzer can be accurate to within 1%. Such accuracy can be achieved, of course, only if samples can be transferred from the scrubber to the chemiluminescent analyzer without loss of NO or NO_X. Figure 2 is a schematic of our experimental setup, diagramming how the chemiluminescent analyzer was connected to the scrubber inlet and outlet.

Our chemiluminescent analyzer was connected to the outlet of the scrubber via a 3.0-meter length of ¼-inch o.d. polyethylene tubing. The chemiluminescent analyzer drew in gas through this tube at a rate of 0.93 L/min. (We measured this rate with a Precision wet test meter.) In comparison, the gas flow rate out of the scrubber during these tests was never less than 1700 L/min, so only a tiny fraction of the gas exiting the scrubber was diverted into the NO/NO_X chemiluminescent analyzer. The relative humidity of the gas as it leaves the scrubber is estimated to be about 85%. This estimate is based on the assumption that the 8-mol/L NaOH aqueous scrubbing liquor obeys Raoult's law. If the temperature of the polyethylene transfer line is less than the temperature within the scrubber, some of the moisture in the exhaust gas might condense within the transfer line, forming aerosols or water droplets on the walls. There is also the possibility that nitric acid aerosols might be present in small amounts in the gas stream exiting the scrubber. Previous measurements have shown that as
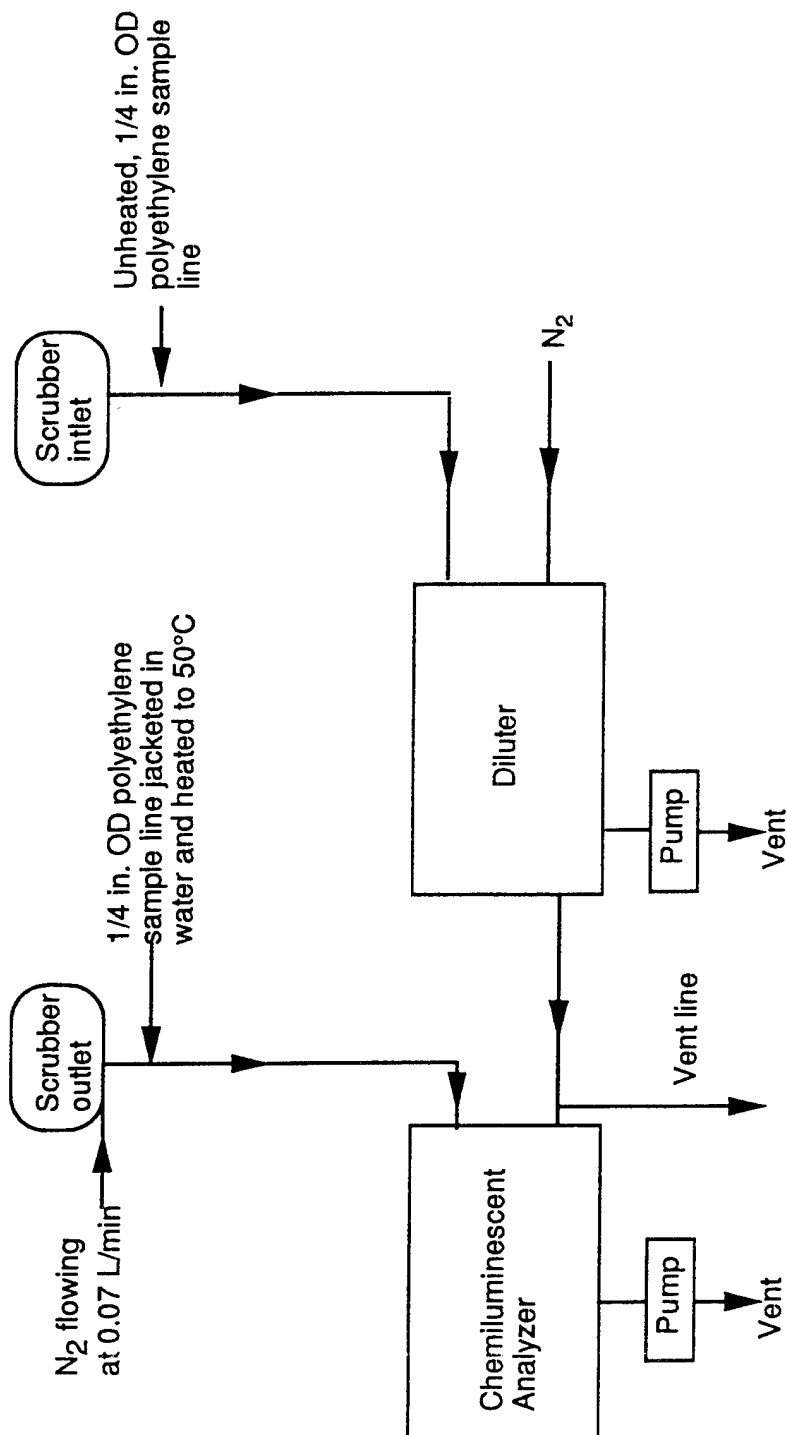
Figure 2. A simplified block diagram showing how the measurements of x_{NOx} and x_{NO} were made. Exhaust gases were pumped directly into the chemiluminescent analyzer; inlet gases were pumped first to a diluter. The diluter delivers more gas than the chemiluminescent analyzer can handle. The rest is vented downwind. The chemiluminescent analyzer is fitted with a second pump, not shown, that keeps its internal reaction chamber at a low pressure. The diluter also has a second pump and a second vent line. Also not shown are the calibrating gases and some ancillary equipment.

the relative humidity in the transfer line approaches or exceeds 100%, the concentration of NO_x decreases and the concentration of NO rises, presumably due to reactions 3, 4, and 5 taking place in the aerosols or droplets that form whenever the relative humidity reaches 100%. The percent decrease in NO_x, of course, depends on the amount of condensation. Just two or three droplets on the walls of the transfer line and an undetermined amount of aerosols in the gas stream have caused a 10% to 50% decrease in NO_x in a transfer line 2 to 4 meters long.[7,8] If precautions are not taken, condensation in the transfer lines would be a frequent occurrence, since the temperature of the scrubbing liquor often exceeds that of ambient air. For example, during compliance testing on 18 Dec 1989,[9] the scrubbing liquor was 81°F, while the ambient air was only 60°F. A gas at 81°F and a relative humidity of 85% will reach a relative humidity of 100% when cooled to just 76°F and will produce copious amounts of condensation when cooled down to 60°F.

We made sure the relative humidity of the gas in the polyethylene transfer line was always much less than 100% by keeping the transfer line heated to a temperature of 50°C. This was done by encasing the ¼-inch o.d. polyethylene tubing within ½-inch OD copper tubing, making a water-tight connection between the ends of the copper tubing and the polyethylene transfer line with Swagelok fittings, filling the space between the two tubes with water, wrapping the copper tubing with heating tape, and heating it to about 50°C. The alternative of simply wrapping the polyethylene tubing directly with heating tape is unsatisfactory because it is nearly impossible to heat the polyethylene uniformly in this way. Polyethylene or any acceptable substitute, such as Teflon, is a thermal insulator, and to get uniform heating, the heating tape has to be wrapped around it uniformly, which is virtually impossible to do. Heating portions of polyethylene or Teflon tubing to a high temperature in hopes that all other portions will be at least 50°C is undesirable. Polyethylene tubing begins to soften at about 65°C; Teflon does not soften until higher temperatures, but Teflon tubing can act like a sponge for NO_2 vapors.

The TECO model 10 chemiluminescent analyzer that we used has two factory-installed inlet ports, both mounted on a back panel of the instrument. As an added precaution to prevent condensation, we moved one of these inlet ports into the interior of the instrument (where the temperature is several degrees above ambient) and attached directly to it the heated transfer line from the outlet of the scrubber. The other inlet port was left on the back panel of the instrument, and the transfer line carrying the dry gas from the scrubber inlet was attached to it.

As a final precaution, a 0.07 L/min stream of dry nitrogen was added to the sample gas just as it entered the transfer line. This was done to prevent condensation from occurring within the chemiluminescent analyzer. (Even though the temperature within this analyzer was above ambient, it was still much less than 50°C). No condensation was observed on the polyethylene or Teflon lines within the analyzer. If condensation had been observed or if there had been any indirect evidence of a condensation problem, the flow of dry nitrogen would have been increased. The dry nitrogen flow was measured throughout the test with a mass flow meter calibrated with the Precision wet test meter. The stream of dry nitrogen diluted the sample gas by about 7.5% ($0.07/0.93 \times 100$), and the measured mole fractions of NO and NO_x were corrected accordingly.

The gas flowing into the scrubber contained about 275,000 ppm NO_X in dry nitrogen (N_2). About 0.6 L/min of this gas was drawn through unheated ¼-inch polyethylene tubing into a TECO model 900 diluter. The model 900 diluter mixed one part scrubber inlet gas with 39 parts dry nitrogen. Dilution was necessary because the maximum amount of NO_X that the chemiluminescent analyzer can measure is 10,000 ppm. The factory-installed particulate filter was removed from the diluter before the start of the test. This filter is unnecessary, and it adsorbs NO_2 like a sponge, decreasing response time, thereby making it impossible to observe fluctuations in the NO_X concentration. The model 900 diluter delivers more gas than the model 10 chemiluminescent analyzer can draw in. The excess was passed through a long length of polyethylene tubing and vented 15 to 20 m downwind from the scrubber. Likewise, the exhaust from the pumps connected to the chemiluminescent analyzer and to the diluter was passed through plastic tubing and vented downwind.

Our chemiluminescent analyzer, like any other chemiluminescent analyzer, has to be calibrated with a gas mixture containing a known concentration of NO_X. We calibrated our analyzer just before the start of the test with an NBS-certified standard of 100 ppm NO in N_2. The calibration was checked at the end of the test and found to be unchanged. We checked this calibration with a Matheson standard of 2430 ppm NO_2 in N_2. Before the start of the test, this standard gave a reading of 2425 $\pm$ 25 ppm NO_X; at the end of the test, this standard gave a reading of 2350 $\pm$ 10 ppm, which is 3% lower than it was at the start of the test. We do not know the reason for this 3% drop in response. The 2430 ppm NO_X in N_2 standard was also used to determine the dilution ratio (40 to 1) of the model 900 diluter that we used.

4. TEST RESULTS

The liquid N_2O_4 is stored at the HSF in a 28,662-gallon tank. The liquid N_2O_4 is always blanketed with gaseous nitrogen N_2 while in storage; consequently, the space in the tank above the liquid N_2O_4 (the head space or ullage) contains a mixture of N_2 and vapors from liquid N_2O_4. Whenever liquid N_2O_4 is added to a partially filled tank, the ullage gases are compresssed by the rising liquid level. When the pressure reaches 35 psig, venting of the ullage gases begins. This venting is termed tank blowdown. The ullage gases, of course, cannot be vented directly into the atmosphere since they contain toxic N_2O_4/NO_2 vapors. The alkaline scrubber at the HSF is designed to remove most of these vapors. The purpose of the 13 Dec 1991 test reported here was to measure the scrubber's efficacy and to determine the maximum acceptable rate at which ullage gases can be passed through the scrubber and into the atmosphere.

The scrubber must protect workers from exposure to N_2O_4 vapors. For this reason, the exhaust from the scrubber is first sent through a 120-ft-long horizontal duct that leads away from the scrubber and then up a 50-ft-long vertical stack before being discharged into the atmosphere at a height of about 75 ft above ground. The scrubber must also meet the stipulations set forth by the Santa Barbara Air Pollution Control District. These stipulations limit the NO_2 emissions from the scrubber to 2.59 lb/hr and 0.216 ton/yr. There is also a requirement that the exhaust plume contain so little NO_2 that it be invisible to the naked eye, or nearly so. Previous tests at other test sites have shown that this means, for a 4-inch-diam exhaust stack, that the mole fraction of NO_2 in the exhaust cannot exceed 600 or 700 ppm.[7,10] When the scrubber exhaust contains more than about 1200 ppm NO_2, the plume out of the exhaust stack has a readily observable brownish color.

Tank blowdown was simulated during the 13 Dec 91 tests by adding N_2 to the ullage gases until the pressure reached approximately 35 psig (3.4 atm absolute). The ullage volume was estimated to be 26,440 gallons, or 100 m^3. The rate at which the ullage gases were vented into the scrubber was controlled with an orifice plate. Two orifices were used: one having a diameter of 0.344 inch (11/32 inch, or 0.873 cm), the other having a diameter of 0.45 inch (or 1.14 cm). The area of the hole in the second orifice plate (1.026 cm^2) was 1.71 times larger than the area in the first plate (0.599 cm^2).

The test with the 0.344-inch-diam orifice lasted 20 min; the exhaust plume during this test was to our eyes colorless. An observer who is certified to conduct Ringleman visual plume assessments could, however, detect a faint color. The test with the 0.45-inch-diam orifice lasted only three minutes. The exhaust plume, as it exited the exhaust stack, was brown with a Ringleman number that exceeded 1.0. The exhaust plume quickly entrained ambient air upon leaving the exhaust stack. This entrained air diluted the plume, making it invisible to the naked eye 5 to 10 meters downwind from the top of the stack. Nevertheless, because the plume was clearly visible near the top of the exhaust stack, the test had to be stopped after 3 min, and in the future, the N_2O_4 storage tank must be vented through the 0.344-inch-diam orifice. A summary of the test data and results is given in Table 1.

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Table 1. Aerospace's Test Data and Results, 13 December 1991

orifice dia (inch)	elapsed time (min)	approx. tank pressure (psig)	approx. NO_x/N_2 flow (SCFM)	approx. N_2 flow (SCFM)	inlet NO_x (ppm)	inlet NO (ppm)	outlet NO_x (ppm)	outlet NO (ppm)
.344	1	35.9	64				970	9
	2	35.6	64	52	280,000	14,400	870	8
	9	33.9	64	53	268,000	13,800	880	9
	18	31.6	64	53	256,000	14,400	860	8
0.450	1	35.6	110	(90)	(275,000)	(14,000)	2160	16
	2	35.3	110	(90)	(275,000)	(14,000)	1675	
	3	35.0	110	(90)	(275,000)	(14,000)	1675	

( ) denotes an estimated or assumed value; see text.
SCFM = standard cubic feet per minute, with standard conditions being $P = 1$ atm and $T = 60°$F. 1 SCFM $\approx$ 1.20 mol/min.

The tank pressure, which could be measured only to 0.5 psig, was recorded every few minutes and plotted as a function of time. The tank pressures given in this Table are from a straight line fit to these measurements.

The flow rate of the NO_X/N_2 gaseous mixture through the 0.344-inch-diam orifice given in Table 1 was computed from measurements of tank pressure as a function of time. The computed average flow rate (~ 64 SCFM) implies that the gas flow through the 0.344-inch-diam orifice was choked, that is, the gas flowed through the orifice at the speed of sound. The gas flow would be expected to remain choked, that is, moving at the speed of sound, until the pressure in the tank drops below about 17 psig. For choked flow, the gas flow rate is proportional to the absolute pressure P of the ullage gas, and the logarithm of this pressure should vary approximately linearly with elapsed time t. (The variation of $\ln P$ with time would be almost precisely linear if gaseous N_2O_4 did not dissociate and if liquid N_2O_4 did not vaporize.) The pressure P dropped from 36.5 psig to 31 psig over the 20 min duration of the test, and a plot of $\ln P$ vs t gave a reasonably straight line, but so did a plot of P vs t. The pressure measurements were accurate enough to give an approximate average flow during the 20-min test (64 SCFM), but not precise enough to determine the variation in the flow during the 20-min test. For this reason, only the average flow rate is reported in Table 1.

It was impossible during the 3-min test with the 0.45-inch-diam orifice even to determine a reliable value for the average flow rate. Instead, it was assumed that the flow through this orifice orifice was 1.71 times greater than the flow through the 0.344-inch-diam orifice since its area is 1.71 times greater. The flow rate so computed is about 14% less than that determined in a previous measurement,[11] made under slightly different conditions.

During the 20-min test with the 0.344-inch-diam orifice, three separate measurements were made of the NO_X and NO mole fractions in the gas vented from the storage tank and entering the scrubber. As shown in Table 1, the NO_X mole fraction dropped from 280,000 to 256,000 ppm during the test, which is a 9% decrease. I am confident that this decrease is real and not a measurement error. There was insufficient time to measure the inlet NO_X and NO mole fractions during the 3-min test with the 0.45-inch-diam orifice. However, it is unlikely that these mole fractions were much different from those measured during the 20-min test.

Table 1 lists the flow rate of N_2 through the scrubber during the 20-min test with the 0.344-inch-diam orifice. The flow rate of N_2 was computed from the measured rate of flow of NO_X/N_2 gaseous mixture, from the measured values of the mole fractions of NO_X and NO in the inlet gas, and from the equilibrium constants for reactions 1 and 8.

The last two columns in Table 1 list the most important results, the mole fractions of NO_X and NO in the gas leaving the scrubber. All other things being equal, the slower the gas flow through the scrubber, the greater the amount of NO_X that will be scrubbed. This is because the slower the gas flow, the longer the gas remains in the scrubber, and so the greater the chance of NO_X removal. The results in Table 1 are largely in accord with this simple picture. The mole fraction of NO_X in the scrubber exhaust gas is, *after the first minute of run time*, about 870 ppm when the gas flow is about 64 SCFM, and 1675 ppm when the gas flow is about 110 SCFM. These measured mole fractions are in agreement with the visual observations of plume color, since a plume with 870 ppm NO_X is expected to be only faintly visible, while a plume with 1675 ppm NO_X should be clearly brown.

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Consequently, not much, if any, of the NO_x in the gas leaving the scrubber was lost or chemically changed in 170-ft long exhaust duct and stack. This may not always be the case. As is pointed out in section 3, the relative humidity of the gas in the scrubber is about 85%. If the walls of the scrubber exhaust duct and stack are just 3 to 5°C cooler than the scrubber liquor, moisture will condense on these walls and aerosols will form in the gas phase. Aerosols can form even when the relative humidity is somewhat less than 100%.[12] The moisture on the wet walls and especially in the aerosols will convert a portion of the N_2O_4/NO_2 in the exhaust to nitric acid (HNO_3) and NO via reactions 3, 4, and 5. Both NO and HNO_3 aerosols are colorless. So under some circumstances, an exhaust duct and stack that are cooler than the scrubber liquor can change a brown exhaust into a colorless plume. Unfortunately, gaseous NO and nitric acid aerosols are toxic, and so the exhaust plume will not necessarily be less harmful, just cleaner looking.

At the start of the 20-min test with the 0.344-inch-diam orifice, the outlet NO_x mole fraction rose from 0 ppm to about 970 ppm within the first minute of run time. Then it dropped to 870 ppm and remained stable thereafter. Likewise, at the start of the 3-min test with the 0.45-inch-diam orifice, the outlet NO_x rose from 0 to 2160 ppm within the first minute, then dropped to 1675 ppm and remained stable thereafter. I have no explanation for the observed overshoots; they have not been observed in previous tests[2-5] at other locations, and they are probably not significant since they last only a minute, while a complete tank blowdown takes much longer. The overshoots are so large that they almost certainly cannot be ascribed to experimental error in the NO_x measurement.

After the first test with flow through the 0.344-inch-diam orifice, the crew responsible for scrubber operations began to purge the scrubber inlet line with gaseous N_2 to flush out the residual NO_x vapors. The NO_x concentration was monitored with the chemiluminescent analyzer during the purge. After 20 min of purging, the concentration of NO_x in the inlet line had barely dropped. Something was obviously wrong. An on-the-spot investigation revealed that an attempt was inadvertently being made to flush out a liquid separator that must have contained a sizable amount of N_2O_4. This separator was bypasssed, and the inlet line was flushed of its NO_x vapors within 13 min.

As is discussed in more detail in the next section, the performance of the OVSS alkaline scrubber at the HSF, as measured during the 13 Dec 91 test, is similar to that observed previously in tests with other NASA/Air Force OVSS alkaline scrubbers.[2-5] A 53 SCFM gas flow containing 870 ppm NO_x carries with it about 2.5 g/min or 0.34 lb/hr NO_x. Consequently, when the 0.344-inch-diam orifice is used, there is no problem meeting the Santa Barbara Air Pollution Control District's requirement that less than 2.59 lb/hr NO_2 be discharged into the atmosphere during scrubber operations.

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5. DISCUSSION AND COMPARISON WITH MEASUREMENTS MADE BY B.T.C. ENVIRONMENTAL, INC.

5.1 Comparing the Inlet NO_X Measurements to Calculated Values

The N_2O_4 oxidizer stored at the HSF is MON-1 N_2O_4, which is N_2O_4 with 1 wt % dissolved NO. As is discussed in Section 2 of this report, NO dissolves in N_2O_4 by reacting with it to form N_2O_3 (reaction 7). Liquid-phase MON-1 N_2O_4 contains only N_2O_4 and N_2O_3; the mole fractions of NO and NO_2 dissolved in this liquid are negligible.[13] Consequently, the mole fraction $x_{N2O3(soln)}$ of N_2O_3 in a N_2O_3/N_2O_4 solution containing w wt% NO is

$$x_{N2O3(soln)} = \frac{w/M_{NO}}{(100-w)/M_{N2O4} + \frac{1}{2}w/M_{NO}} \tag{13}$$

where M_{NO} and M_{N2O4} are the molar masses of NO and N_2O_4. The mole fraction of N_2O_4 is

$$x_{N2O4(soln)} = 1 - x_{N2O3(soln)} \tag{14}$$

Substitution of $w = 1.0$ in Eqs. 13 and 14 gives $x_{N2O3} = 0.0305$ and $x_{N2O4} = 0.9695$.

Even though there are essentially only two species present in pure liquid MON-1, in the vapor phase above this liquid, there are four species, N_2O_4, N_2O_3, NO_2, and NO, as well as the nitrogen diluent. The concentrations of NO and NO_2 are not negligible in the gas phase because, as is disscussed in Section 2, in the gas phase, a sizable fraction of the N_2O_4 and N_2O_3 molecules dissociate into NO_2 and NO (reactions 1 and 8). The partial pressures of N_2O_4, N_2O_3, NO_2, and NO are completely specified by the following four equilibrium constants:

$$(P_{NO2})^2/x_{N2O4(soln)} = K_I = \exp(33.254 - 10537/T) \tag{15}$$

$$P_{N2O4}/x_{N2O4(soln)} = K_{II} = \exp(12.109 - 3661/T) \tag{16}$$

$$P_{NO}(x_{N2O4(soln)})^{1/2}/x_{N2O3(soln)} = K_{III} = \exp(-14.68 + 4048/T) \tag{17}$$

$$P_{N2O3}/x_{N2O3(soln)} = K_{IV} = \exp(-14.479 + 4555/T) \tag{18}$$

where the Ks are equilibrium constants, P_B is the partial pressure of species B in atm, and T is the absolute temperature in kelvin. The partial pressure of species B is equal to its mole fraction x_B times the total pressure P_{tot}:

$$P_B = x_B P_{tot}. \tag{19}$$

The total pressure comprises not just the sum of the partial pressures of the nitrogen oxides, but also the pressure of the nitrogen diluent. The equilibrium constants in Eqs. 15 - 18 are functions of temperature alone; they do not depend on the total pressure. The temperature-dependent expressions for K_I, K_{II}, K_{III}, and K_{IV} given in Eqs. 15 - 18 are valid for $262 < T < 300$ K ($12°$ to $80°$F).

Pressures calculated using these expressions match the very accurate and precise measurements of Chang and Gokcen[13] and the extraordinarily accurate measurements of Giauque and Kemp.[14,15]

The chemiluminescent analyzer measures x_{NOx}. Equation 12, in Section 3, gives an expression for x_{NOx} in terms of the mole fractions of NO, NO_2, N_2O_3, and N_2O_4; substitution of Eq. 19 into Eq. 12 gives Eq. 20, which is an expression for x_{NOx} in terms of the partial pressures of the nitrogen oxides and the total pressure, P_{tot}:

$$x_{NOx} = (P_{NO} + P_{NO2} + 2P_{N2O3} + 2P_{N2O4})/(P_{tot} + P_{N2O3} + P_{N2O4}) \qquad (20)$$

A chemiluminescent analyzer also measures the mole fraction that NO would have if all the N_2O_3 and N_2O_4 were dissociated. This mole fraction, $x_{NO(meas)}$, differs slightly from the actual mole fraction of NO, x_{NO}:

$$x_{NO(meas)} = (x_{NO} + x_{N2O3})/(1 + x_{N2O3} + x_{N2O4}) = (P_{NO} + P_{N2O3})/(P_{tot} + P_{N2O3} + P_{N2O4}) \qquad (21)$$

Dividing Eq. 20 by Eq. 21 gives an expression for the ratio of NO to NO_x that would be measured by a chemiluminescent analyzer:

$$x_{NO(meas)}/x_{NOx} = (P_{NO} + P_{N2O3})/(P_{NO} + P_{NO2} + 2P_{N2O3} + 2P_{N2O4}) \qquad (22)$$

Figure 3 gives x_{NOx} as a function of temperature, calculated using Eq. 20 and the equilibrium constant given in Eqs. 15-18. Before the start of each test, nitrogen was added to the ullage above the liquid N_2O_4 until the pressure reached about 35 psig. The calculation in Figure 3 is for a uniform, equilibrium mixture of ullage gases above liquid MON-1 N_2O_4 pressurized with nitrogen to a total pressure of 35 psig. Before entering the scrubber, the ullage gases expanded through an orifice. The pressure downstream of the orifice (and upstream of the scrubber) was just above ambient (0 psig). During the expansion from 35 psig to 0 psig, the composition of the gas changed: the mole fractions of N_2O_4 and N_2O_3 decreased and the mole fractions of NO_2 and NO increased, because a lower pressure leads to increased dissociation. However, the value of x_{NOx} did not change because x_{NOx} is defined as the combined mole fraction of NO_2 and NO if all the N_2O_4 and N_2O_3 were dissociated. As is shown in Table 1, on December 13th, Aerospace measured x_{NOx} to be about 280,000 ppm when the total pressure was about 35 psig. This would imply that the temperature of the liquid N_2O_4 was about 51°F if the nitrogen oxide vapors and the diluent nitrogen were well mixed.

As ullage gas is vented through the 0.344-inch orifice, the remaining gas is cooled a bit because it expands to replace the gas that has left. This could lead to some N_2O_4 condensation, which would collect in the liquid separator upstream of the orifice. If such condensation occurred, the mole fraction of NO_x would have decreased with time, which is what was observed (see Table 1). A measurement of the vapor temperature would help prove or disprove this explanation for the observed small decrease in inlet NO_x with time.

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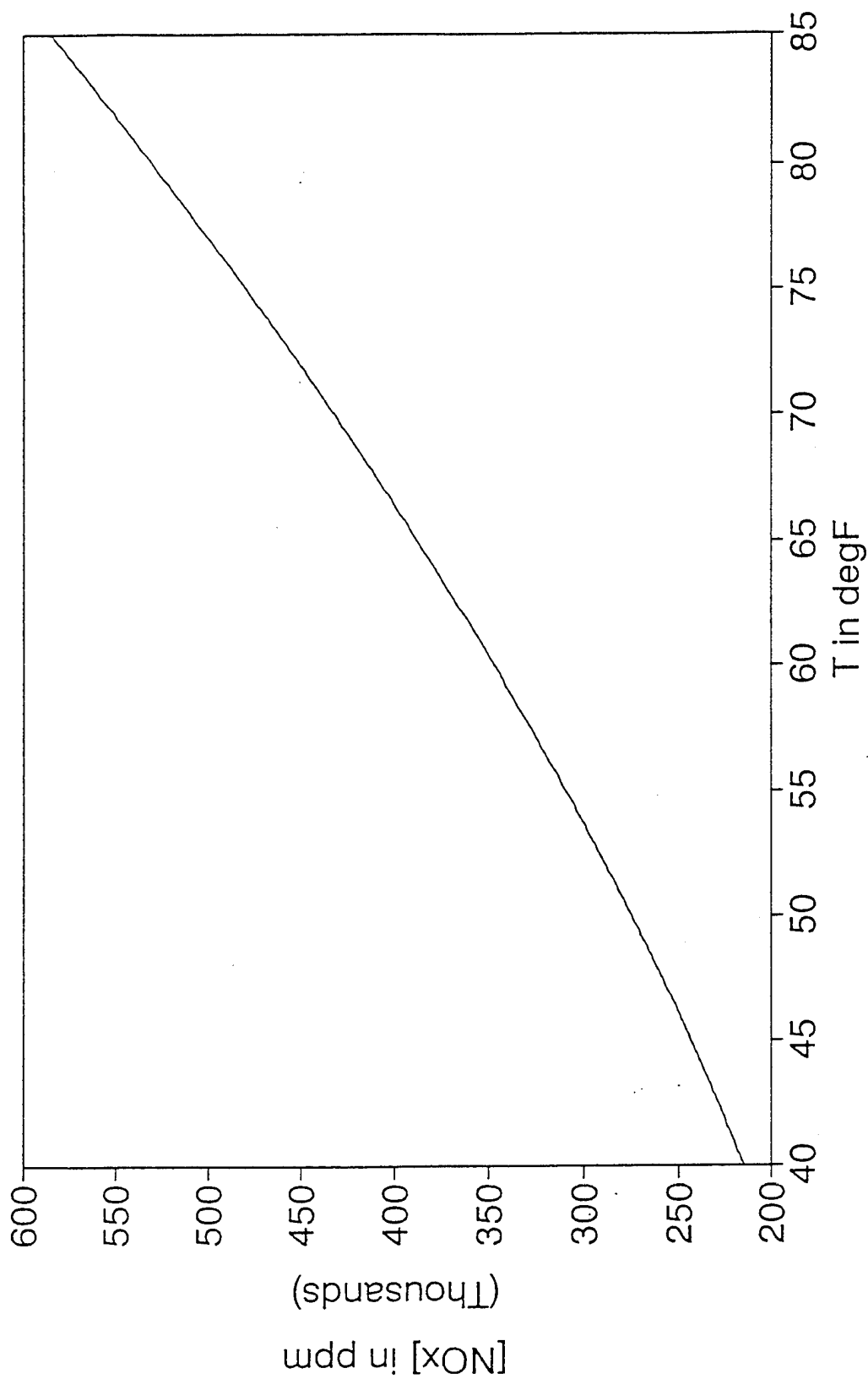
Figure 3. An equilibrium calculation of the mole fraction x_{NOx} of gaseous NO_X in the ullage above liquid MON-1 N_2O_4. The liquid N_2O_4 is pressurized with an inert gas, such as nitrogen, until the combined pressure of the nitrogen oxides and diluent is 35 psig at sea level or 3.38 atm absolute. The calculations were performed assuming that the liquid and the gas above it are at the same temperature and that the diluent gas and the nitrogen oxide vapors are well mixed. The calculated values of x_{NOx} are accurate to within a few percent.

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The temperature of the N_2O_4, liquid or vapor, was unmeasured, but 51 °F is not an unreasonable temperature for the liquid. The average December temperature in nearby Santa Maria is 52 °F, and it is not unreasonable to expect the average temperature at the HSF to be very similar and the liquid N_2O_4, because of its large thermal mass, to be at a temperature not too much different from the average ambient temperature. In contrast, as is discussed below, measurements made a few days later (on 17-18 December 1991) by B.T.C. Environmental, Inc., did not always give consistent values for the inlet NO_X mole fraction or reasonable values for the temperature of the MON-1 liquid. Current regulations of the Santa Barbara Air Pollution Control District require periodic testing of the scrubbers at VAFB. During future tests, it would be desirable to make thermocouple measurements of the temperatures of the MON-1 liquid and its vapor. It would then be possible, using the information in Figure 3, to make a more accurate comparision between the expected inlet NO_X mole fraction and the measured value. A large discrepancy between measured and expected NO_X mole fractions would suggest a problem with the measurements that might need correcting or perhaps an inadequacy in the assumption that the nitrogen diluent and the nitrogen oxide vapors are well mixed. Conversely, agreement between predictions and measurements would be evidence that the measurements being made are accurate.

As can be calculated from the data in Table 1, for the gases in the scrubber inlet stream, the ratio $x_{NO(meas)}/x_{NOX}$ varied between 0.051 and 0.056. For MON-1 containing exactly 1.0 wt% NO, the expected value of $x_{NO(meas)}/x_{NOX}$, as computed from Eqs. 14-17 and Eq. 19, is 0.050 ± 0.001 for any temperature between 50 °F and 75 °F. The fairly close agreement between measurement and calculation is further evidence that the measurements of x_{NOX} and $x_{NO(meas)}$ made by Aerospace are accurate. B.T.C. Environmental did not make measurements of x_{NO} during the scrubber tests on 17 - 18 December 1991.

The calculated chemical composition of the gas above liquid MON-1 at 51 °F, pressurized with nitrogen to 35 psig, is $x_{N2} = 0.813$, $x_{N2O4} = 0.129$, $x_{NO2} = 0.0417$, $x_{NO} = 0.0138$, $x_{N2O3} = 0.0019$. The calculated flow for a gas of this composition through a 0.344-inch-diam orifice having a discharge coefficient of 0.85 is 62 SCFM for an average upstream pressure of 34 psig. The measured flow rate was approximately 64 SCFM, which is very good agreement. A discharge coefficient of 0.85 is typical for a thin orifice,[16] but this coefficient could be a little larger or somewhat smaller than 0.85. Consequently, even though the measured flow rate into the scrubber agrees with calculations, a flow rate a few percent greater or 10% to 15% smaller would also be consistent with calculations because the discharge coefficient of the orifice plate is not accurately known.

5.2   Comparing Outlet NO_X Measurements to the Results of Previous Measurements

Previous measurements[2-5] and theoretical analysis[17] have shown that the mole fraction of NO_X in the scrubber's exhaust is, to a fair approximation, proportional to the flow rate of the nitrogen diluent through the scrubber and nearly independent of the initial concentration of NO_X entering the scrubber, provided this initial concentration exceeds about 50,000 ppm. For example, if the concentration of NO_X entering the scrubber were reduced by a factor of 5, from 250,000 ppm to 50,000 ppm, while keeping the nitrogen diluent flow constant, the mole fraction of the NO_X in the

scrubber's exhaust would not change significantly. This perhaps surprising result is a consequence of the fact that the rate of NO_2 removal depends on the square of the NO_2 concentration. When the NO_2 concentration is large, the rate of scrubbing is *very* large, and in a *very* short time the concentration of NO_2 is reduced to a much lower level. Regardless of the initial NO_2 concentration, the concentration of NO_2 in the scrubber soon reaches about 10,000 ppm, because the rate of scrubbing when the NO_2 concentration exceeds 10,000 ppm is large, and the rate when this concentration exceeds 50,000 ppm is exceedingly large. The rate-limiting process in the scrubber is the removal of NO_2 when its concentration is low (below about 10,000 ppm). The slower the flow rate of nitrogen diluent through the scrubber, the more time will be available for reducing NO_2 from about 10,000 ppm to some lower level, and the lower will be the mole fraction of NO_2 in the scrubber's exhaust.

The rate of removal of NO in the scrubber is proportional to the product of the NO and NO_2 concentrations. Provided $[NO_2] > > [NO]$, the mole fraction of NO in the scrubber's exhaust will likewise be nearly independent of the NO concentration in the gas entering the scrubber.

Previous tests[2-5] have shown that when the nitrogen diluent flow is 50 SCFM, the mole fraction of NO_X in the scrubber's exhaust is about 1000 ppm, and when the nitrogen flow is 100 SCFM, the NO_X mole fraction is about 2000 ppm. In the test of 13 Dec 91, the NO_X mole fraction measured in the scrubber's exhaust was about 900 ppm when the N_2 flow was 50 SCFM and was about 1700 ppm when the N_2 flow was 90 SCFM (see Table 1). The agreement between the results of these measurements and previous measurements is as good as could possibly be expected.

5.3 Comparing Aerospace's Measurements to Similar Measurements made by B.T.C. Environmental

On 17 and 18 December 1991, during the week following the measurements made by Aerospace, described above, the alkaline scrubber at the HSF was again tested. There were three tests over the 2-day period. Test conditions for each of these three tests matched the conditions of the first test on December 13th, in that the 28,000-gallon tank contained the same amount of liquid N_2O_4 as it did on that date, was pressurized to about 35 psig, and was vented through the small (0.344-inch-diam) orifice into the scrubber. During these tests, the gas exhausting from the scrubber was colorless or nearly so.

During the December 17 and 18 tests, B.T.C. Environmental measured the NO_X flow rates into and out of the scrubber. Aerospace made no measurements. B.T.C. Environmental was a subcontractor to West Coast Environmental, Inc., which provided management services and technical expertise. West Coast Environmental, in turn, was a subcontractor to Jacobs Services Company and Environmental Management Consultants, Inc., who in turn were contractors working directly for the U.S. Air Force at VAFB. The results of the measurements made by B.T.C. Environmental were submitted to the Santa Barbara Air Pollution Control District in partial fulfillment of the requirements for obtaining a permit from that organization to operate the scrubber. The permit was granted, and the scrubber has been operating successfully since then.

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Table 2 gives the results of B.T.C. Environmental's measurements, as determined from data given in Reference 18. As shown in Table 2, before the start of each of the three tests, the 28,000-gallon tank in which the N_2O_4 was stored was pressurized to about 35 psig with nitrogen. Each test lasted 30 min, and in each test, the pressure in the 28,000-gallon storage tank dropped to 29 psig after 20 min of gas flow, and to 27 psig after 30 min. The average nitrogen flow out of the 28,000-gallon tank and into the scrubber was about 47 SCFM in all three tests. As intended, the experimental conditions for the three tests were just about identical; however, the measured amounts of NO_x entering and leaving the scrubber were quite different. The measured inlet NO_x mole fraction varied from 318,000 to 571,000 ppm, and the outlet NO_x mole fraction varied even more, from 470 to 1300 ppm. The inconsistency in these results suggests there may have been experimental errors in determining the NO_x mole fraction. The nitrogen flow measurements, which are consistent, are probably accurate.

B.T.C. Environmental measured the average velocity of the gas flow out of the scrubber with a pitot tube. The flow rate of the gases leaving the scrubber can be determined from their velocity and the cross-sectional area of the exhaust duct. The nitrogen flow rate is determined by assuming that the gas leaving the scrubber was nearly saturated with water vapor, which would make its composition about 98% nitrogen and about 2% water vapor and nitrogen oxides. Pitot tube measurements of flow velocity can be highly accurate. The measurements made by B.T.C. Environmental are uncertain, however, by about ±10%, due to the imprecision in the readings of the water manometer that was used to measure the difference between the total and static pressures. Aerospace estimated a nitrogen flow of 52 to 53 SCFM. B.T.C. Environmental's measurements imply that this flow was 10% lower, or 47 SCFM. The measurements made by B.T.C. Environmental may be more accurate than those made by Aerospace, but this is not completely certain. However, the difference between the measurements is fairly small.

B.T.C. Environmental measured NO_x mole fractions using EPA method 7D, which involves bubbling a portion of the gas flow through an alkaline permanganate solution for 20 or 30 min and subsequently analyzing the solution in the laboratory by ion chromatography for nitrate ion concentration. As with the chemiluminescent analyzer, EPA method 7D detects nitric acid, both in the gas phase and in aerosols, as NO_x.

B.T.C. Environmental's measurements of the NO_x mole fraction in the gas entering the scrubber during the first 20 min of each test varied from a low of 318,000 ppm in the second test to a high of 571,000 ppm in the third test. Sample collection time was 20 min, and the gases flowing into the scrubber were sampled only once during each 30-min test. B.T.C. Environmental could not have known that the values of x_{NO_x} measured in succesive tests were so different until days later when the laboratory analyses were complete. The lowest value of x_{NO_x} measured, 318,000 ppm, is about 15% higher than that measured by Aerospace, but still is a very reasonable value for x_{NO_x}. As shown in Figure 3, this mole fraction is the expected mole fraction of NO_x when the temperature in the 28,000-gallon storage tank is 56°F. Such a temperature is not unreasonable, since the average ambient temperature is typically around 52°F in December. The vapor pressure of liquid MON-1

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Table 2. B.T.C. Environmental's Test Data and Results, 17 and 18 December 1991

test	tank pressure start of test (psig)	tank pressure after 20 min (psig)	tank pressure after 30 min (psig)	20-min av. N_2 flow (SCFM)	20-min av. inlet NO_x (ppm)	30-min av. outlet NO_x (ppm)
1	35	29	27	47	360,000	470
2	34.5	29	27	47	318,000	630
3	35	29	27	45	571,000	1300
av. of 3 tests						800

The NO_x mole fractions were determined by sampling the gas flow for 20 or 30 min and subsequently analyzing the sample collected in the laboratory by ion chromatography. No measurements were made of the mole fraction of nitric oxide, NO. The mole fraction of NO_x in the inlet gas stream was determined from a 20-min collect. The mole fraction of NO_x in the outlet stream was determined from a 30-min collect since the concentration of NO_x in the outlet stream is smaller.

The average nitrogen flow was calculated directly from the pitot-tube measurements, assuming, as B.T.C. Environmental assumed, that the pitot tube was placed so as to measure the average gas velocity in the exhaust duct.

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N_2O_4 at 56°F, as calculated from Eqs. 15-18, is 0.73 atm. B.T.C. Environmental measured the nitrogen flow during test 2 to be 47 SCFM when the pressure in the storage tank was 35 psig or 3.38 atm absolute. If the temperature in the storage tank was 56°F, the total flow out of the the tank was $(47)(3.38)/(3.38 - 0.73) = 60$ SCFM. Consistent with this value, Aerospace estimated a total flow of 64 SCFM during its measurements on December 13th.

B.T.C. Environmental's measurement of 318,000 ppm NO_x in the inlet gas stream is a reasonable result, just as reasonable as Aerospace's measurement of 270,000 ppm a week earlier. During the first test, B.T.C. Environmental measured the inlet NO_x mole fraction to be 360,000 ppm. This measurement is much less reasonable, inasmuch as 360,000 ppm is the expected NO_x mole fraction when the temperature in the storage tank is 62°F, which is a higher temperature than seems probable. During the third and final test, B.T.C. Environmental measured the inlet NO_x mole fraction to be 571,000 ppm. This is the mole fraction that would be expected if the temperature in the storage tank were 84°F, which is clearly impossible. The vapor pressure of MON-1 at 84°F is 1.51 atm. B.T.C. Environmental measured the nitrogen flow during test 3 to be 47 SCFM when the pressure in the storage tank was 35 psig or 3.38 atm absolute. If the temperature in tank were 84°F, the total flow out of the tank would have been $(47)(3.38)/(3.38 - 1.51) = 85$ SCFM. This is an impossibly large flow to pass through a 0.344-inch-diam orifice when the upstream pressure is 35 psig. The maximum flow under these conditions could not exceed 74 SCFM, even if the orifice had an impossibly large discharge coefficient of 1.00. It is clearly impossible that the storage-tank ullage could have contained 571,00 ppm NO_x in the gas phase.

The inlet gas could have contained 571,000 ppm NO_x only if there to had been a *dense* fog of N_2O_4 droplets within the storage tank and these droplets had passed through the liquid separators upstream of the orifice and then passed through the orifice itself. Variations in temperature can produce a fog, but a temperature in excess of 84°F would have been required to produce a fog dense enough to explain the measurements of B.T.C. Environmental during test 3. This could not have happened since the temperatures everywhere were always below 70°F. A dense fog could have conceivably been present in the 28,000-gallon storage tank during test 3, if for some reason, the nitrogen diluent, while being added to this storage tank before the test, did not mix well with the N_2O_4 vapors already present in the tank, but instead mostly compressed these vapors into a smaller volume, thereby forcing some fraction of the vapors to condense. However, the measured nitrogen flow in test 3 was about the same as it was in the previous two tests, which indicates that mixing was about the same in all three tests, as would be expected. Also there is no apparent reason why a dense fog of N_2O_4 should have formed in test 3, but not in the other tests. The inlet NO_x measurement on test 3 is probably erroneous; the cause of the error is unknown.

The NO_x mole fraction in the gas exiting the scrubber was measured by B.T.C. Environmental using the same wet chemical method that was used to measure inlet NO_x mole fraction, except that the sample collection time was 30 min instead of 20 min. Only one sample was collected per 30-min test. The measured mole fractions of NO_x in the scrubber exhaust varied from a low of 470 ppm in the first test to a high of 1300 ppm in the third test, even though the nitrogen flow in each of the

three tests was measured to be nearly identical. As is discussed above, theory predicts, and previous measurements have confirmed, that the NO_X concentration in the scrubber's exhaust should depend almost entirely on the nitrogen flow rate and be almost independent of the inlet NO_X mole fraction whenever this mole fraction exceeds about 50,000 ppm. Aerospace measured an outlet mole fraction of about 900 ppm, which is in good agreement with previous measurements made by others. It's a mystery why B.T.C. Environmental measured low mole fractions (470 and 630 ppm) during the first two tests and a high mole fraction (1300 ppm) during the third test. In two important aspects, however, the measurements of Aerospace and B.T.C. Environmental are in agreement. First, B.T.C. Environmental noted that the gas from the scrubber, when exhausted into the atmosphere, was "very, very slightly visible," which matches Aerospace's observations. Second, the three-test average value of NO_X in the gas exiting the scrubber was 800 ppm in B.T.C. Environmental's measurements. This average was reported to the Santa Barbara Air Pollution Control District and is fortuitously in substantial agreement with the 875 ppm measured by Aerospace. In my opinion, Santa Barbara County received the correct information.

5.4   Improving Measurement Accuracy in Future Compliance Tests

If B.T.C. Environmental had performed only two tests instead of three, the average measured value of NO_X in the scrubber's exhaust would have been only 550 ppm, which would have implied that the scrubber operates much better than it actually does. In a 1989 measurement of the performance of the scrubber at VAFB's Space Launch Complex 4 East (SLC-4E), B.T.C. Environmental[9] measured NO_X mole fractions that were about a factor of 15 too low. B.T.C. Environmental made more accurate measurements this time because at Aerospace's recommendation, an improved gas-sampling system was used. The Santa Barbara Air Pollution Control District requires periodic measurements of scrubber performance. Accurate measurements can be consistently made by using a chemiluminescent analyzer and by following procedures described in this report.

Both the chemiluminescent method used by Aerospace and the wet-chemical method used by B.T.C. Environmental are EPA-approved methods for measuring NO_X mole fractions. The wet-chemical method requires a subsequent laboratory analysis of collected samples by ion chromatography. I have used both a chemiluminescent analyzer and an ion chromatograph. Both instruments are capable of precise and accurate measurements; however, I have found that it is far easier and much quicker to obtain accurate results with a chemiluminescent analyzer. In addition, the chemiluminescent method has three advantages over wet-chemical analysis: (1) results are obtained in real time, (2) both NO and NO_X are measured, and (3) several measurements of NO and NO_X can be made during a 20- or 30-minute test. Many things can go wrong in a test. Often it is hard to know something is wrong with a test or with a measurement until the results become available. Real-time measurements often allow errors to be found quickly and corrected. Measuring NO as well as NO_X provides additional information that can be of value in assessing the validity of the measurements. Measurements, for example, that indicate that more NO than NO_2 is exhausting from the scrubber imply that the scrubber is not operating properly, or more likely that there is moisture in the gas-sampling lines, and this moisture is converting NO_2 to NO via reactions 3, 4, and 5. Large fluctuations in x_{NO_X} or x_{NO} under supposedly steady-state conditions imply either that the conditions are not really steady

state or that there is a measurement error. Discordant results from supposedly identical tests also indicate a problem. If B.T.C. personnnel knew in real time they were obtaining descordant results, they would have almost certainly tried to determine the cause of this problem and corrected it, if possible.

B.T.C. Environmental determined the nitrogen flow through the scrubber by measuring the gas flow velocity in the scrubber's exhaust duct with a pitot tube. The gas flow exiting the scrubber is about 98% nitrogen; the remainder is water vapor and nitrogen oxides. A direct measurement of the nitrogen flow is highly desirable because the amount of NO_X discharged from the scrubber into the atmosphere is highly dependent on the nitrogen flow rate. A pitot tube gives the difference between the total and static pressures in the gas flow, from which the gas velocity is computed. This pressure difference was measured by B.T.C. Environmental using a water manometer. A pressure transducer would have been more accurate and much easier to use. Real-time measurements of the flow velocity can be made by sending the output of the pressure transducer and the output from a thermocouple measuring the gas temperature into a PC data acquisition board. A 286 PC fitted with an inexpensive data acquisition board would be adequate for this purpose. The PC would be programmed to compute the flow velocity and the nitrogen flow rate in SCFM from the signals sent by the pressure transducer and the thermocouple. Whether measured in real time or computed after each test, the nitrogen flow should be determined in future tests directly from a pitot measurement, rather than indirectly from the decrease in the tank pressure, as was done by Aerospace. Determining the nitrogen flow from the decrease in tank pressure is imprecise because (1) the pressure can be measured to only 0.5 psig with the present gauge, (2) the tank pressure decreases not just because N_2 is flowing out of the tank, but also because NO_X is flowing out as well, and (3) because a not easily predicted amount of liquid MON-1 N_2O_4 vaporizes during a test to replace some of the N_2O_4 that is being vented.

Two other recommendations for better testing are given elsewhere in this report. These recommendations are (1) follow procedures similar to those employed by Aerospace to eliminate the possibility of moisture in the scrubber's sampling lines and (2) measure the temperature of the liquid MON-1 N_2O_4 in the storage tank and the temperature of its vapors.

5.5   Increasing Speed and Performance with an Add-On Alkaline-Sulfite Scrubber

An alkaline scrubber, such as the OVSS at the HSF, is very efficient in terms of percentage NO_X removed whenever the concentration of NO_X is large, 100,000 ppm or more. In such cases, well over 95% of the NO_X is scrubbed. However, an alkaline scrubber cannot reduce the NO_X concentration to near zero. This is because the rate of scrubbing is proportional to the square of the NO_X concentration, and when the $[NO_X]$ within the scrubber becomes small, the scrubber becomes inefficient. Adding a fifth tower to the four-tower OVSS scrubber, or making each of the existing towers larger, would not reduce the concentration of NO_X in the exhaust much below its present value of 1000 to 2000 ppm. The amount of NO_X can be reduced from several thousand ppm to less than 100 ppm with an alkaline-sulfite scrubber only a quarter the size of the present alkaline scrubber.[19] In an alkaline-sulfite scrubber, the rate of scrubbing is proportional to the first power

of the NO_2 concentration. Scrubbing appears to be as rapid as the rate at which gaseous NO_2 is transported to the liquid scrubbing solution. The IIT Research Institute has designed an alkaline-sulfite scrubber[20] to serve as an add-on to the existing Oxidizer Vapor Scrubbing Systems at the HSF and at the launch sites. With this add-on scrubber, tank venting at the HSF could easily proceed at 200 SCFM instead of at 50 SCFM nitrogen flow.

5.6   Venting the Storage Tank at a Faster Rate by Modifying the Scrubber's Exhaust Duct
The scrubber has a 170-ft-long exhaust duct to carry the exhaust vapors up and away from the scrubber. These vapors are discharged into the atmosphere at a height of about 75 ft at a distance of about 120 ft from the scrubber. The first few feet of the scrubber's exhaust duct has a diameter of 4 inches. Then the duct narrows to a diameter of 2 inches for the next 100 ft and then expands back to 4 inches for the last 70 ft. The diameter of the duct at the point at which the vapors are discharged into the atmosphere is 4 inches.

As discussed earlier in this report, when the gas flow into the scrubber was about 64 SCFM, the light brownish color of the plume at the end of the exhaust duct was barely visible. But, when the gas flow was 110 SCFM, the plume was clearly visible. Since visible plumes are prohibited by the Santa Barbara Air Pollution Control District, the scrubber has had to operate at a 64 SCFM inlet flow.

The plume is most clearly visible just as it exits the exhaust duct. Downwind from the exhaust duct, the plume rapidly entrains air, becoming more dilute and more difficult to see, and soon becomes invisible. The visibility of an NO_2 plume is approximately proportional to the diameter D of the plume times the concentration of NO_2 in the plume:

$$\text{plume visibility} \propto D[NO_2] \tag{23}$$

The diameter of the plume as it exits the exhaust duct is equal to the diameter of the duct. The mole fraction of NO_2 in the exhaust gases depends only on the efficiency of the scrubber, not on the diameter of its exhaust duct. A decrease in the duct diameter will force the gases to flow more rapidly through the duct and will increase the backpressure, but will not change the mole fraction of NO_2 in the exhaust duct, nor will it change the NO_2 concentration at the end of the duct. Consequently, the smaller the diameter of the duct, the greater the mole fraction of NO_2 the plume can carry without being visible. When the inlet gas flow was 64 SCFM, the outlet NO_x mole fraction was about 870 ppm, almost all of which was NO_2. When the inlet flow was 110 SCFM, the outlet NO_x or NO_2 mole fraction had almost doubled to about 1675 ppm (see Table 1). To the first approximation, a 2-inch-diam plume containing 1675 ppm NO_2 should be no more visible than a 4-inch-diam plume containing 875 ppm NO_2. Consequently, it is probable that scrubber operation with an inlet flow of 110 SCFM would have resulted in a nearly invisible exhaust plume if the diameter of the exhaust duct had not been increased from 2 inches to 4 inches or if this diameter had been reduced back to 2 inches before the gases were discharged into the atmosphere.

The analysis given in the preceding paragraph is somewhat simplified in that it assumes the viewer is looking horizontally straight across the plume, rather than at an angle that lies somewhere between the horizontal and vertical. The viewing angle, of course, depends on the location of the viewer relative to the base of the exhaust stack. The analysis in the preceding paragraph is also only approximate even for a horizontal viewing angle, because Eq. 23 is only approximate. Nevertheless, decreasing the exhaust duct diameter will significantly decrease the visibility of the plume. It may not be possible to operate the scrubber at 110 SCFM with a 2-inch-diam duct, but it certainly will be possible to operate at a higher inlet flow than 64 SCFM. The advantage of operating at a higher flow is obvious: vent time would be decreased and the storage tanks could be filled more quickly. The disadvantage is that about twice as much NO_x would be released into the atmosphere, even though the plume would be invisible and the rate at which NO_x would be released (~ 8.3 g/min or 1.1 lb/hr) would still be well below the limit of 2.59 lb/hr set by the Santa Barbara Air Pollution Control District. The cost of reducing the diameter of the exhaust duct from 4 inches to 2 inches is almost negligible. All that would be required is to join a few feet of 2-inch-diam pipe to the existing 4-inch-diam duct.

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